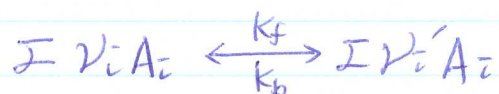


## < Chemical Kinetics II >

An elementary reaction



$$(\nu'_i - \nu_i) \overline{RR}_f''' = \frac{d[A_i]}{dt} = (\nu'_i - \nu_i) k_f(T) \prod_i [A_i]^{\nu_i}$$

$$(\nu_i - \nu'_i) \overline{RR}_b''' = \frac{d[A_i]}{dt} = (\nu_i - \nu'_i) k_b(T) \prod_i [A_i]^{\nu'_i}$$

$$\overline{RR}_f''' = -\overline{RR}_b''' \text{ @ equilibrium.}$$

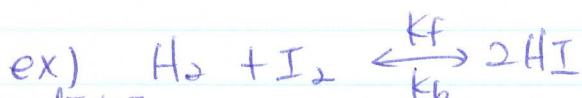
$$\frac{k_f}{k_b} = \frac{\prod [A_i]^{\nu'_i}}{\prod [A_i]^{\nu_i}} \equiv K_c \text{ concentration}$$

$$K_p = K_c (\overline{RT})^{\Delta n}, \quad \Delta n = \sum_{i=1}^N (\nu'_i - \nu_i)$$

equilibrium constant.

\*  $K_p$  is a function of  $T$  only.

\* Equilibrium constant are generally known more accurate than the rate coefficient.



$$\frac{d[HI]}{dt} = \underbrace{2k_f [H_2][I_2]}_{\text{''}} - \underbrace{2k_b [HI]^2}_{\text{''}}$$

$$A_i = HI, \quad \nu'_i - \nu_i = 2 \quad \nu_i - \nu'_i = -2$$

$$\frac{d[HI]}{dt} = 0 \text{ @ equilibrium.}$$

$$\therefore 0 = 2K_f [H_2]^* [I_2]^* - 2k_b [HI]^{*2}$$

\*: equilibrium concentration

$$\therefore \frac{k_f}{k_b} = \frac{[HI]^{*2}}{[H_2]^* [I_2]^*} = K_c$$

$$\frac{d[H_2]}{dt} = 2k_f[H_2][I_2] - 2\frac{k_f}{k_c}[HI]^2$$

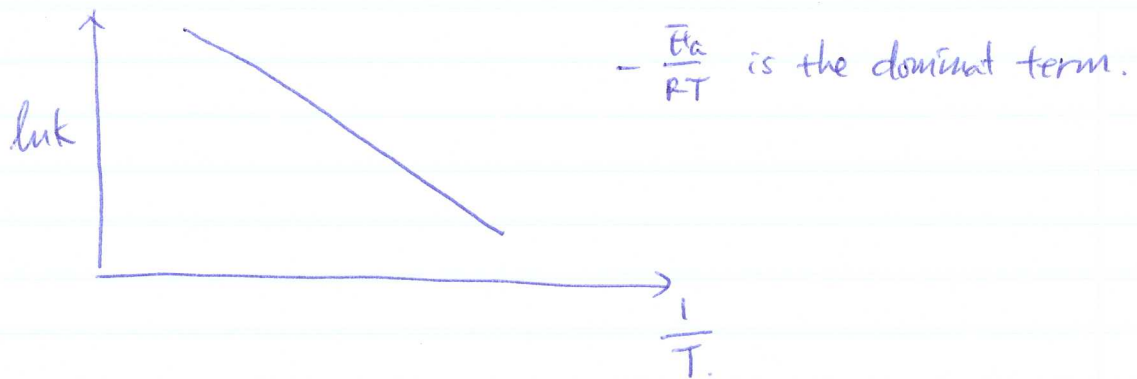
\* Arrhenius form of rate coefficient.

$$k = AT^b \exp\left(-\frac{E_a}{RT}\right)$$

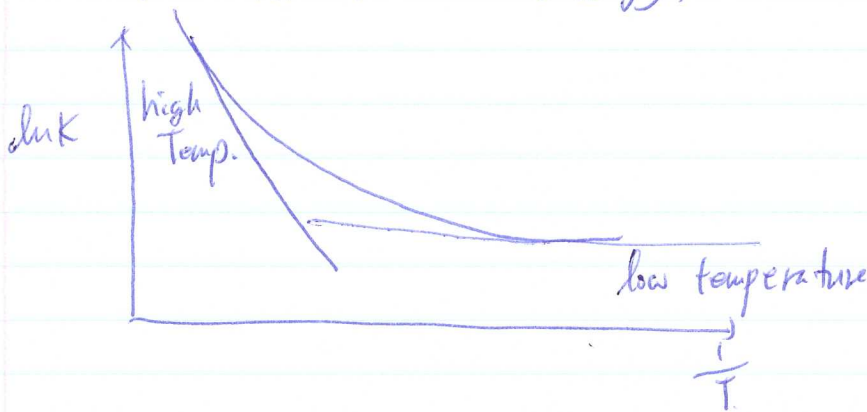
- typically,  $0 \leq b \leq 1$ ,  $E_a > 0$  with some exceptions.
- usually, highly exothermic reactions have low activation energies.

$$\ln k = \ln A + b \ln T - \frac{E_a}{RT}$$

→ if  $E_a$  is sufficiently large



→ with low activation energy.



## \* Pressure dependence

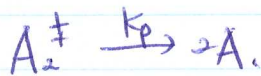
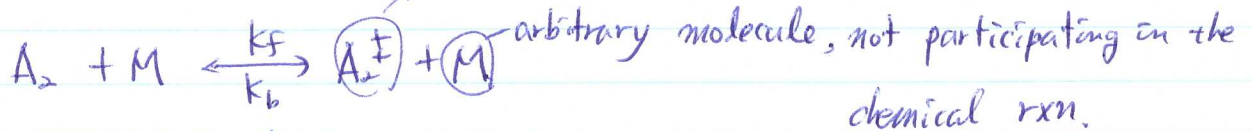
→ dissociation rxn.



↑

no collision?

activated state



$$\frac{d[A_2]}{dt} = -k_f [A_2][M] + k_b [A_2^\ddagger][M]$$

$$\frac{d[A_2^\ddagger]}{dt} = k_f [A_2][M] - k_b [A_2^\ddagger][M] - k_p [A_2^\ddagger]$$

Assume  $A_2^\ddagger$  is very reactive (fast destruction)

→  $[A_2^\ddagger]$  is very small and nearly constant.

$$\Rightarrow \frac{d[A_2^\ddagger]}{dt} = 0$$

$$[A_2^\ddagger] = \frac{k_f [A_2][M]}{k_b [M] + k_p}$$

$$-\frac{d[A_2]}{dt} = \frac{k_f k_p [A_2][M]}{k_b [M] + k_p} = k_{app} [A_2]$$

\*  $[M]$  is proportional to total pressure.

i) at high pressure,  $k_b [M] \gg k_p \Rightarrow k_{app} = \frac{k_f k_p}{k_b} = k(T)$

→ the rxn is pseudo-first order and  $A_2$  is in equilibrium with  $A_2^\ddagger$

ii) at low pressure,  $k_b [M] \ll k_p \Rightarrow k_{app} = k_f [M]$ , rxn order is two,  
 $\therefore k_{app} \propto \text{Pressure}$

### \* Kinetic Approximation

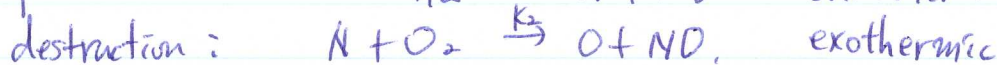
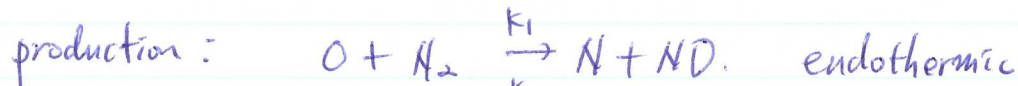
o Quasi-steady state (QSS)

→ QSS eliminates species from rate laws

→ QSS applies to a species not to a particular reaction.

Most often, QSS is applied to a radical whose concentration is very small and which is formed by a slow, endothermic rxn and removed by a fast thermoneutral or exothermic rxn.

ex) N-atom



$$\frac{d[N]}{dt} = k_1 [O][N_2] - k_2 [N][O_2]$$

QSS applied to N  $\Rightarrow \frac{d[N]}{dt} = 0 \Rightarrow$  the rate eqn for N is eliminated

$$\therefore [N]_{QSS} = \frac{k_1 [O][N_2]}{k_2 [O_2]}$$

$$t_{QSS} = \frac{[N]_{QSS}}{k_1 [O][N_2]} = \frac{1}{k_2 [O_2]} \leftarrow \text{time scale of QSS.}$$

$\Downarrow$   
time required for  $[N]_{QSS}$  production

o Partial Equilibrium (PE)

→ PE pertains to one or several rxns in the rxn mechanism.

→ rates of forward and reverse rxns are equal.



$$k_f [O][H_2] = k_b [OH][H] \quad \frac{[OH][H]}{[O][H_2]} = \frac{k_f}{k_b} = K_c = K_p$$

$\Rightarrow$  PE most often applies to fast, energetically neutral rxns.